Photothermal Lens Spectrometry in Small Cylinders

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A novel apparatus for performing photothermal lens spectroscopy is described. The apparatus uses a low-volume cylindrical sample cell, a chopped or pulsed excitation laser, and a continuous probe laser. The full volume of the sample is irradiated with constant, e.g., non-Gaussian, irradiance beam produced by the excitation laser. Constant irradiance excitation source does not directly produce the photothermal lens element in the sample. The lens element is formed by thermal diffusion from the irradiated sample volume, through the sample cell walls. Under continuous irradiation, thermal diffusion results in a parabolic temperature change profile.

The most important aspect of this experiment arrangement is that articats due to excited state refractive index changes, volume changes, etc. do not affect the signal. Although the refractive index change may depend on the partial refractive index and partial molar volume of transient species, these changes do not result in a photothermal lens element. By monitoring both the central portion and the full probe laser beam, the apparatus can compensate for transmission changes due to bulk density, refractive index, or absorbance changes.

This talk will briefly outline the model used to relate the heat transfer and the photothermal effect to experimental observation. Experiments to verify the operation of the apparatus are performed with dicyclopentadienyl iron (FeCp2) in ethanol. Photothermal lens signals are processed in the usual fashion. The resulting signals are found to be relatively linear and reproducible. The experimental photothermal lens enhancement is found to be that predicted from theory, within experimental error.